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DEVELOPMENT OF A NEW BIO-KINETIC MODEL FOR ASSESSING THE ENVIRONMENTAL PROPERTY OF MILITARY HYDRAULIC FLUIDS

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ABSTRACT

The U.S. Army Tank-Automotive Research. Development and Engineering Center (TARDEC) is actively developing biodegradation technologies that can be used to minimize waste stream of Petroleum, Oils, and Lubricant (POL) products utilized in the current and future combat systems. As part of these efforts, a bio-kinetic model was developed to predict the biodegradability of lubricants including hydraulic fluids. This model can predict a biodegradability of lubricant based on a composition analysis within a short period. The advantages of this model are its predictable capability and excellent correlation with results obtained from the conventional biodegradation tests. This paper presents the results of development of a bio-kinetic model, its composition technique, and correlation study with the conventional biodegradation tests and the field demonstrations, and its applicability to the military hydraulic fluids.

1. INTRODUCTION

Petroleum based hydraulic fluids have been used in various hydraulic systems for many decades. These fluids are usually toxic and not readily biodegradable. A common factor in most hydraulic systems is the potential for leakage and the possibility of spillage of fluid during storage and use. The generation of the hazardous wastes by petroleum based or synthetic fluids result in both short and long term liabilities in terms of costs. The DoD Hazardous Waste Minimization (HAZMIN) Policy mandate that all DoD installations must reduce the quantity or volume and toxicity of hazardous waste generated by POL products wherever economically, practicable, and environmentally necessary. To achieve the HAZMIN goals, research and development efforts are being directed to develop new or improved HAZMIN techniques and processes.

To preserve the environment, there has been an increasing interest to use Environmentally Acceptable (EA) Hydraulic Fluids in environmentally sensitive areas such as construction, forestry, and agricultural. EA hydraulic fluids are currently defined as non-toxic and readily biodegradable products [Rhee, 2002]. These types of fluids are originally formulated with renewable oils such as rapeseed, sunflower, corn, soybean, canola, and synthetic esters. One of concerns in these EA fluids is how to evaluate their environmental properties such as the biodegradability under laboratory environments.

Biodegradation is a natural process caused by the action of microorganisms in the presence of oxygen, nitrogen, phosphorous, and trace minerals. Organic pollutants can support microbial growth and are converted into a series of oxidation products that generally conclude with carbon dioxide and water. In a previous study, it was found that the inherent biodegradability of a lubricant depends to a large extent upon its molecular structure and composition [Cookson, 1995]. Typically, straight-chain aliphatic compounds (i.e., alkanes, cycloalkanes) are easily degraded. Simple aromatic compounds are usually slowly degradable and contain toxicity. Polymetric materials are among the most resist to microbial attack. It is also known that oils derived from renewable resources are more biodegradable than petroleum based oils. In addition, the water solubility or dispersability of petroleum based products, their molecular sizes, pH of solution, types of materials, temperature, total dissolved solids, and their toxicity, affect their biodegradability. Among them, it is strongly believed that the molecular structure and low toxicity may play a major role in the biodegradation of lubricant products.

A number of biodegradation tests have been developed for evaluating the biodegradability of lubricants. These biodegradation tests were designed to determine the degree of aerobic aquatic biodegradation of fully formulated lubricants or their components on exposure to inoculums under controlled laboratory conditions. All of these tests can measure the biodegradability of lubricants based on oxygen uptake or carbon dioxide production of microorganisms (inoculums). Recently, ASTM D-2 Subcommittee 12 on Environmental Standard of Lubricants has developed several biodegradation test methods (ASTM D 5864, ASTM D 6731, and ASTM D 6139) for evaluating the biodegradability of petroleum based and renewable based lubricants [ASTM standard, 1997, 2005]. Their test procedures are very similar to each other and simulate the biodegradation process used in the waste treatment center. But these tests require a long testing

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time (28 days), the knowledge of microorganisms, and skilled manpower in some cases. In addition, they have very poor test precision due to the various and multiple inoculums sources. For these reasons, they are very difficult to use in petroleum laboratories for assessing the biodegradability of lubricants.

To resolve these difficulties, a new Bio-kinetic model has been empirically developed to predict the biodegradability of lubricants using a modified ASTM compositional analysis technique and the fundamental microbiological theory [Rhee, 2005]. This bio-kinetic model requires compositional analysis data of lubricants and some of formulation information related to the types of base oils used in the lubricants. The advantages of this model is (1) its predictable capability for the biodegradability of lubricants within a day and (2), its excellent correlation with results obtained from ASTM D 5864 (Modified Stun Test). To further validate this model, a correlation study was conducted using various types of hydraulic fluids including renewable based fluids with two popular biodegradation tests (Modified Stun test, Respirometer) and CES Company's CO_2 evolution test [CES, 2004]. This comparison study is essentially needed to determine whether a conventional biodegradation test or the bio-kinetic model can serve as a screening test for assessing biodegradability of fluids.

2. DEVELOPMENT OF BIO-KINETIC MODEL

A bio-kinetic model is a new methodology to predict the biodegradability of a lubricant. This model has been developed based on the fundamental microbiology theory, and the compositional analysis of lubricant. This bio-kinetic model does not require any biodegradation test apparatus and inoculums. It can predict the biodegradability of lubricant within a day, and has a good correlation with the ASTM D 5864 biodegradation test using the round robin sample for ASTM D 5864 [ASTM, 2005]. The bio-kinetic model is described as follow:

$$B(t) = B(1) + \frac{0.49}{\ln(6.8 \times ECB^{-2.38})} \ln t$$

$$where\ :$$

$$ECB = \sum_{a}^{b} (\eta_a C_a + \eta_b C_b)$$

$$B(1) : 0.01$$

B (t) is expressed as a cumulative biodegradability of sample for elapsed time t. B (1) was found to be close to the first day of biodegradation which can be determined experimentally. The Effective Composition for Biodegradation (ECB) is sum of all saturate and ester fractions. C is represented by amount of composition of each type of oil and η is its ECB coefficient.

In this bio-kinetic model, the ECB value can be calculated using the ASTM D 2549, Separation of Representative Aromatics and Nonaromatics Fractions of High-Boiling Oils by Elution Chromatography. The schematic diagram of this test apparatus is shown in Figure 1. The test method tends to provide information on the separation and determination of representative aromatics and non-aromatics fractions from the petroleum based hydrocarbon oils using a chromatographic column. In a trial test, it was found that this procedure was not applicable to renewable based oils due to their inseparability problem. For this reason, some modification was made to analyze renewable products and its changes that are listed in Table 1. Mainly, the modified procedure has a four-step process instead of a three-step process. The first step eluted non-aromatic materials using a pentane solvent. Then, non-polar based aromatics were eluted using a mixture of 50 % pentane and 50 % toluene instead of diethyl ether. In step 3 process, the esters or related products were eluted using a diethyl ether. The polar-based aromatics were eluted in the step 4 process.

Table 1. Modified ASTM D 2549 Procedure

Process	Modified ASTM D 2549	
Step 1	Pentane	Non-aromatics (saturate, mineral oil, PAO)
Step 2	50 % pentane+50% toluene	Non-polar based aromatics
Step 3	Diethyl ether	Esters, acid, waxes
Step 4	Chloroform/Ethyl alcohol	Polar based aromatics

The modified procedure was designed based on the dielectric constant of solvents and their eluting characteristics. It was fully evaluated using known samples prior to the tests. The major advantage of this test is its small sample size requirement (2g), and its good test precision. Also, it was found that this procedure can not differentiate between some chemicals that are eluted by same solvent such as mineral oil and polyalphaolefin (PAO) oils, or esters. In this case, the identification of oils can be directly obtained from oil manufacturers or through additional tests (i.e., Gas Chromatography (GC) or Infrared Spectroscopy (IR)).

Generally, the biodegradability of hydrocarbon based oils depends on the types of materials and chemical structures. For this reason, an adjustment was essentially needed for this compositional analysis to determine the effective composition for the biodegradation (ECB) of lubricants. Table 2 lists the ECB coefficient for each type of oil. These coefficients were calculated based on the data obtained from biodegradation tests and range from 1 for the renewable ester to 0.01 for the Petroleum based ester type. In this calculation, ECB is sum of all fractions of saturate and esters except for all aromatic fractions that are considered as toxic materials.

Table 2. ECB Coefficients for Oils

Type of Base oil	ECB Coefficient (η)
Mineral oil	0.3
PAO 2*	0.8
PAO 4*	0.6
PAO 6 or above*	0.4
Natural esters	1
Renewable based polyol ester or diester	0.8
Petroleum based ester types	0.01

* Viscosity grades for polyalpaolefin (PAO)

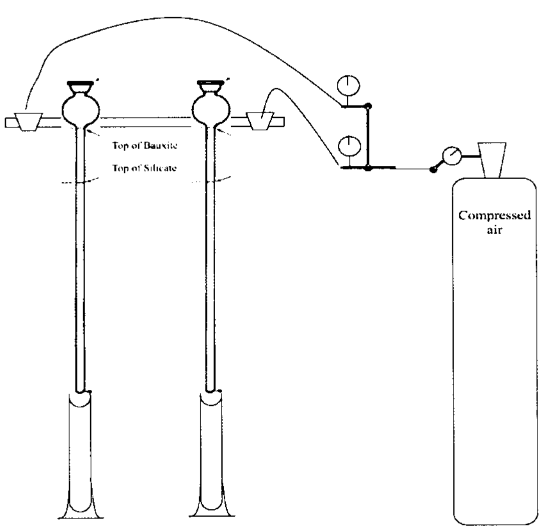

Figure 1. ASTM D 2549 Test Apparatus

3. TEST SAMPLES

The hydraulic fluids are currently formulated with various types of oils and additives to meet specific applications. The four most common types of hydraulic fluids are mineral oil, synthetic esters, polyalphaolefin (PAO), and vegetable oils. Currently, these types of fluids are widely used in conventional hydraulic systems. To determine the applicability of bio-kinetic model to the hydraulic fluids, nine typical hydraulic fluids were selected from available commercial and military products. They consists of three biobased fluids qualified under MIL-PRF-32073 [Military specification, 2001], two commercial biobased fluids (i.e., soybean, rapeseed), two PAO- based fluids, a mineral based oil, a polyol-ester blended fluid based fluid, and a PAO-ester blended fluid qualified under MIL-PRF-46170 [Military specification, 2001]. These samples were fully formulated by the lubricant companies with different types of base oils, viscosity grades, and chemical additives. Most of these fluids are military specification products and currently being used for the hydraulic applications. These products are listed in Table 3 with their identifications.

Table 3. Test Sample

Code	Type of base oil	ISO classification	Identification
A	Mineral oil	100	SAE 15W-40
B	Soybean	46	Commercial HF*
C	Canola	46	MIL-PRF-32073 Grade 4
D	Canola	46	MIL-PRF-32073 Grade 4
E	PAO 2	2	Commercial HF
F	PAO 6	6	Commercial HF
G	Rapeseed	32	Commercial HF
H	Polyol ester +mineral	22	MIL-PRF-32073 Grade 2
I	PAO 4 +diester	22	MIL-PRF-48170

*Hydraulic Fluid

4. LABORATORY TEST RESULTS

To assess the bio-kinetic model, nine different types of hydraulic fluids were tested using the bio-kinetic model. The kinetic model was originally designed to calculate the biodegradability of fluids based on the ECB value and the carbon conversion of the test sample within a short period. The ECB of each fluid was actually measured using the modified ASTM D 2549 compositional analysis technique that provides an excellent test precision. This technique eluted four different types of chemical compositions from a fluid. It consists of non-aromatics compounds such as saturates (mineral oils, PAO), non-polar based aromatics, ester groups, and polar based aromatics. Generally, the aromatic compounds tend to reduce the biodegradability of fluids due to their structure and toxicity. In this bio-kinetic model, the aromatic compositions were ignored for ECB calculation. Table 4 shows the compositional analysis of tested fluids and their ECBs. It clearly indicated that each fluid has a different chemical composition and ECB. The high composition of ester gave a high ECB value that is reflected to the high biodegradability of that fluid. In the other case, it was found that the 2 cSt PAO fluid (Code E) composed of 98.8 % saturates and its ECB coefficient is 0.8 that is much higher than that of mineral oil (0.3). Table 4 also shows that the predicted biodegradability of tested fluids who ranges from 32.8 to 79.0 %. It appears that this analytical technique is not only providing good biodegradability differentiation, but information regarding how one can improve the biodegradability of fluids based on their compositional analysis.

Table 4. Test Results obtained from Bio-kinetic Model

Code	Alkanes or Saturate, %	Non-polar aromatics, %	Ester, Acid, or Wax, %	Polar aromatics, %	ECB*	Predicted biodegradability
A	82.5	13.5	1.4	1.7	0.26	32.8
B	24.5	2.2	67.9	5.4	0.75	64.0
C	3.49	2.57	90.56	3.38	91.6	77.8
D	17.53	1.32	77.45	3.69	0.82	69.3
E	98.8	0.47	0.05	0.7	0.79	67.0
F	99.0	0.07	0.1	0.8	0.4	40.8
G	0.07	1.00	92.95	5.98	0.93	79.0
H	17.5	1.32	77.5	3.7	0.83	70.0
I	68.7	2.9	27.7	0.7	0.55	51.0

* Effective composition for the biodegradation

5. CORRELATION TO CONVENTIONAL BIODEGRADATION TESTS

To make a correlation between bio-kinetic model and conventional biodegradations, the laboratory biodegradation tests were conducted using ASTM D 5864 and ASTM D 6731 test method. Although these biodegradation tests use identical test solutions and inoculums, their measuring techniques of the biodegradability are not same. All of these biodegradation tests require a 28 day exposure period. Figure 2 shows the typical biodegradation profiles of the conventional biodegradation tests and bio-kinetic model for canola based EA fluid (Code D). Table 5 summarizes the biodegradation test results of the tested fluids. Data obtained from bio-kinetic model are also presented in this table to provide a comparison with the conventional biodegradation tests. It is noted that these results were determined based on triplicate test results in order to increase reliability of test data and are expressed as percentage of the maximum (theoretical) carbon dioxide evolution of each sample or oxygen consumption of microorganisms in each test. In these tests, the biodegradability of hydraulic fluids ranges from 30.1 to 84.8 % for 28 days. It is quite evident that the EA hydraulic fluids provided a higher biodegradability than a conventional petroleum based hydraulic fluid. In addition, a 2 cSt PAO based fluid also provided a good biodegradability similar to those of vegetable - based fluids. As expected, a 6 cSt PAO based fluid does not provide a good biodegradability. These results clearly indicated that the biodegradability of fluids also depend on their polymetric structure. Data obtained from the bio-kinetic model provided good correlation with those of the conventional biodegradation tests.

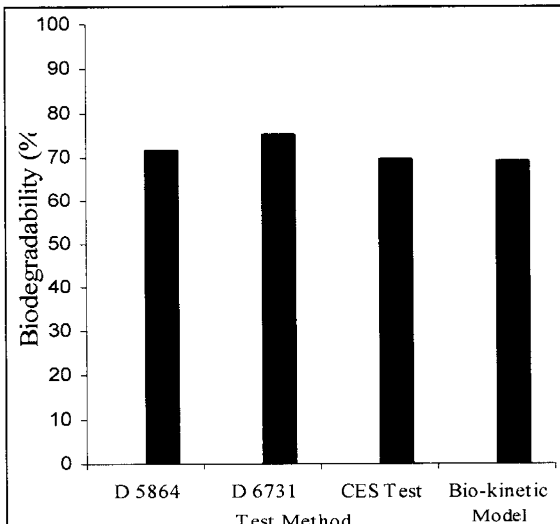

Figure 2. Biodegrability of Canola based MIL-PRF-32073 Hydraulic Fluid

ASTM D 5864 biodegradation test is a version of the Organization for Economic Co-Operation and Development (OECD) 301 B, Modified Stun Test that closely simulates the waste water biodegradation conditions. This test was designed to determine the degree of aerobic aquatic biodegradation of lubricants on exposure to inoculums under laboratory conditions. In this test, the biodegradability of a lubricant is expressed as the percentage of maximum carbon conversion under well-controlled conditions for a period of 28 days. The test apparatus consists of four separate units: the free carbon dioxide air system, biodegradation batch reactor, a carbon-dioxide collector and a titrator. This test apparatus can be easily constructed by the testing laboratory. Most of these components involve regular laboratory glassware (i.e., flasks, etc.). This test apparatus is considerably less expensive than the other types of biodegradation tests (i.e., Respirometer). For the biodegradation test, the five test stock solutions for the test medium were prepared to provide nutrition for microorganisms. These stock solutions were Ammonium Sulfate solution, Calcium Chloride solution, Ferric Chloride solution, and Magnesium. It should be noted that these solutions do not contain any carbon material in order to avoid an extra source of carbon dioxide production. Canola cooking oil was used as a positive controller to verify the microorganism's performance during the test. In addition, the initial carbon content of the test lubricants was measured to establish the maximum theoretical biodegradability of that lubricant. The sewage microorganism from a local waste water treatment plant was used as inoculums in this test. The test was performed for 28 days under dark environment, and the titration for carbon-dioxide cumulation was performed every day for the first ten days and then every other day for the remaining 18 days or until a plateau of carbon-dioxide evaluation was reached. This test has been widely used for many decades by industry and is considered as a reliable biodegradation test. The disadvantages of this test are its poor precision due to the various of inoculums sources and unknown microorganisms' behavior as well as long test times. In addition, this test requires skilled manpower and sufficient laboratory space. Currently, the ASTM D 6046, Hydraulic Fluids for Environmental Impact specifies that the persistence designation of the readily biodegradability is Pw 1 and must be greater than or equal to 60 % of CO_2 evolution in 28 days. Compared with ASTM D 5864 test, the bio-kinetic model does not need the biodegradation test apparatus and inoculums. Table 5 shows their data to be very equivalent to each other. In addition and more importantly, the bio-kinetic technique can reduce the test time from 28 days to 1 day.

Table 5. Biodegradation Test Results

Code	ASTM D 5864	ASTM D 6731	CES CO_2 Evolution Test	Bio-kinetic Model
A	30.1	36.6	24.1	32.8
B	67	63.4	73.7	64.0
C	72.3	75.3	74.1	77.8
D	71.7	75.2	69.7	69.3
E	71.2	78.4	61.3	67.0
F	51.0	57.3	53.2	40.8
G	77.0	84.8	80.2	79.0
H	66	76.6	66.2	70.0
I	51.9	51.3	47.8	51.0

ATSM D 6731 Biodegradation test is another version of OECD 301F, The Manometric Respirometry Test and is known as the modified Biochemical Oxygen Demand (BOD) Test. This closed respirometer test was also designed to determine the degree of biodegradability of lubricants or their components in an aerobic aqueous medium on exposure to an inoculums under laboratory conditions. The test apparatus of ASTM D 6731 biodegradation test is shown in Figure 3. Unlike the ASTM D 5864 test, the biodegradation of a lubricant is determined by measuring the oxygen consumption of microorganisms instead of the carbon conversion of the test sample. This approach was developed based on the assumption that a large amount oxygen uptake of microorganisms indicates more microorganisms' growth or generation and takes more carbon conversion of the test sample leading to carbon dioxide production by an enzyme process. For this reason, the respirometer test is currently considered as an indirect biodegradation test of lubricants, and its biodegradability is expressed as the percentage of maximum oxygen consumption under well-controlled conditions for a period of 28 days.

Figure 3. ASTM D 6731 Biodegradation Test Apparatus (CES Respirometer)

The test apparatus of this test method is a well designed automatic system and requires less manpower. In this test, the oxygen consumption is measured based on the pressure drop of the manometer, which produces a signal that results in the electrolytic generation of oxygen. The sample and medium preparation is almost identical to ASTM D 5864 test sample. The advantages of this method are less manpower required and its closed system that is suitable for evaluating the biodegradation of volatile lubricants. The disadvantage is its indirect measurement of biodegradation of lubricants and its poor test precision. Because of its measuring technique and the cost of test apparatus, this method is not widely utilized within industry. Currently, the ASTM D 6046, Hydraulic Fluids for Environmental Impact specifies that the readily biodegradability of fluid (classification: Pw1) in this test must be greater than or equal to 67 % of O_2 consumption in 28 days. This value is a little higher than that of ASTM D 5864 test because of its total oxygen consumption of microorganisms including biomass production. In this study, the test results were also very comparable with those obtained from the bio-kinetic model.

The CES respirometer apparatus has an option to measure carbon dioxide evolution directly during a respirometer test. In this option, the microorganisms consume oxygen from the respirometer and produce carbon dioxide. Then, this carbon dioxide is trapped in an absorbent solution (i.e., Sodium Hydroxide) and measured by a CO_2 sensor instead of a titration. Even though this technique is very similar to that of ASTM D 5864 test, the test results were much closer to those of ASTM D 6731 because of its closed system that can minimize the loss of carbon dioxide during the biodegradation process. This optional test is not yet developed as a standard test method, but can be considered as a closed automatic ASTM D 5864 test. The advantage of this test over the ASTM D 5864 test is in its automatic system, but it still has a test precision problem. Generally, the closed biodegradation system produces a higher biodegradability of the tested fluids than those of semi-open system.

To determine the correlation between biodegradation tests including bio-kinetic model, the data were analyzed to find the correlation coefficient (r^2) using a statistic method. Table 6 shows their correlation coefficients were found to be from 0.87 to 0.95. It appears that the bio-kinetic model gave a good agreement with the selected biodegradation tests. Typically, the bio-kinetic model gave an excellent correlation to the ASTM D 5864 tests. Both ASTM D 6731 and CES biodegradation test also have a good agreement with those of ASTM D 5864 test. Table 6 clearly shows that data obtained from the biodegradation tests correlate to the Bio-kinetic Model. A typical correlation curve is shown in Figure 4. Therefore, the bio-kinetic model can be also used to predict the biodegradability of hydraulic fluids within a short period. Currently, ASTM D-2 Subcommittee 12 on Environment is reviewing this bio-kinetic model to adopt as an ASTM biodegradation test method.

Table 6. Correlation Coefficient (r^2) between Bio-kinetic Model and conventional biodegradation tests

	Bio-kinetic Model
ASTM D 5864	0.95
ASTM D 6731	0.87
CES CO_2 evolution test	0.87.

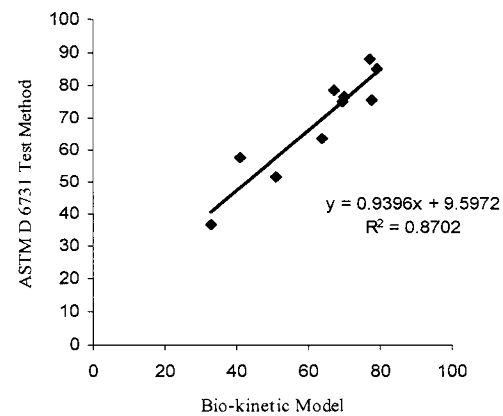

Figure 4. Correlation between Bio-kinetic model and ASTM D 6731

6. FIELD DEMONSTRATION

In 1999, TARDEC had conducted a field biodegradation test to verify the laboratory biodegradation results at the bioremediation site of Fort Hood, TX [Wright and Rhee, 1999]. Three samples (B, C, and G) selected for this study have been tested with other fluids using a modified Fort Hood's remediation procedure. For the test, the samples were mixed with soil and then, plowed and tilled in order to increase homogeneity. No fertilizer and microbes were applied except for water. Soil samples were obtained on a monthly basis and analyzed for total carbon content using the EPA method 413.2, Spectrophotometric, Infrared for Total Hydrocarbon from Wastes. The test results have clearly shown the rapid biodegradability of these biobased fluids within 6 months. The data obtained from the field biodegradation test were plotted in Figure 5 and demonstrated a good correlation to the bio-kinetic model and laboratory biodegradation tests used in this study.

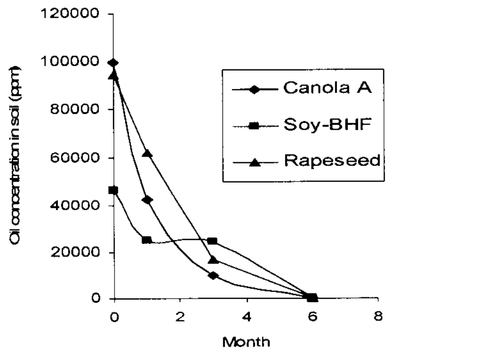

Figure 5. The Results of Field Biodegradation Test

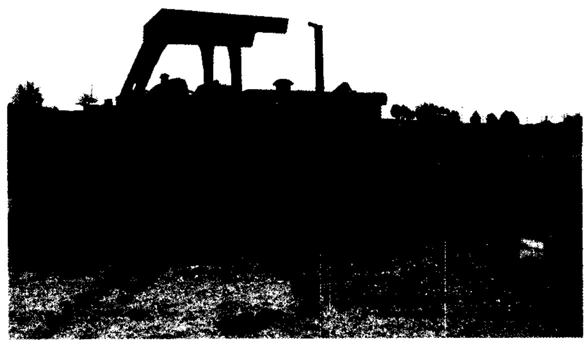

Figure 6. BHF Field Demonstration at Fort Leonard Wood

As a part of the development of EA hydraulic fluids, TARDEC is currently conducting the second field demonstration to validate MIL-PRF-32073 fluids using ten pieces of military construction equipment (i.e., Bulldozers, Cranes, Loader, Graders, Scrapers) at Fort Leonard Wood, MO. In this demonstration, fluid samples (C, D, and H) selected for this study are also being tested with other two MIL-PRF-32073 fluids. All of the tested construction equipment was originally using SAE 15W-40 oil. This construction equipment was used daily for their routine operation and military exercise. The evaluation criteria used in this demonstration were their field performance (i.e., thermal stability, oxidation, evaporation, wear, corrosion, seal compatibility, etc.) and environmental performance (i.e., biodegradability, toxicity). The duration of this field demonstration was encompass a year testing period. Quarterly, all equipment and fluids were inspected (i.e., seal leaking, parts failure, fluid level etc.) and a small sample was also collected from each equipment for laboratory evaluation. The biodegradability of tested fluids was monitored using the bio-kinetic model. In interim results, MIL-PRF-32073 fluids selected did not give any abnormal behavior and clearly demonstrated the acceptable performance equivalent to the SAE 15W-40 oil for the last nine months. In addition, it did not show any biodegradation in the fluid reservoirs during this period [Rhee, 2006]. This implied that the hydraulic fluids can only be biodegraded under certain environmental conditions (i.e., soil or water). The laboratory test results obtained from field samples also clearly supported these test results.

7. CONCLUSIONS

On the basis of the work completed to date, the bio-kinetic model was fully evaluated using nine different types of hydraulic fluids and compared with the conventional biodegradation tests. This bio-kinetic model provided excellent correlation with results obtained from the conventional biodegradation tests. In addition, it reduced significantly testing time from 28 days to one day and can easily predict the biodegradability of fluids without the handling of microorganisms. Therefore, the bio-kinetic model can be used for predicting the biodegradability of fluids as a screening test. The results of this study are summarized with the following findings:

1. The bio-kinetic model gave good correlation with the conventional biodegradation tests (i.e., ASTM D 5864, ASTM D 6731, CES CO_2 evolution test). Their correlation coefficients (r^2) were found to be from 0.87 to 0.95.
2. Modified ASTM D 2548 test was able to analyze the compositions of fluids and provided an excellent test precision. But, it can not differentiate between mineral oils and PAO oils and between renewable ester and non-renewable ester. It requires pre-information of base oil types from oil companies or other techniques (i.e., IR, GC).
3. The effective composition for biodegradation (ECB) gave a good correlation with the biodegradability of fluids. In addition, it can provide vital information on how to improve the biodegradability of fluids.
4. ASTM D 5864 biodegradation test gave a good agreement with ASTM D 6731 respirometer test, but its results were slightly lower than those of the respirometer due to its manual operation and semi-opening system. In addition, it provided very poor

precision like the other biodegradation tests due to the various inoculums sources.

5. CES biodegradation test is an optional CO_2 evolution test of CES closed respirometer and gave a good agreement with ASTM D 5864 test, but its results were very similar to those of the respirometer test. It appeared that the ASTM D 5864 test tends to lose some of CO_2 production due to its semi-opening test apparatus. Thus, the CES CO_2 evolution test can be considered as an automatic ASTM D 5864 biodegradation test.

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